This was found to be the case. The curve of the beam from scale No. 46·3 of the spectrum (about λ 5613) was found to be straight from the origin. Those of beams of greater refrangibility were at first concave to the axis of abscissæ, those of less refrangibility convex; but all had become straight before an intensity of 1/60 of an amyl acetate lamp at 1 foot had been reached.

III. "On certain Ternary Alloys. Part V. Determination of various Critical Curves, and their Tie-lines and Limiting Points." By C. R. Alder Wright, D.Sc., F.R.S., Lecturer on Chemistry and Physics in St. Mary's Hospital Medical School. Received November 19, 1891.

The triangular method of graphical representation suggested by Sir G. G. Stokes, and described in Part IV ('Roy. Soc. Proc.,' vol. 49, p. 174), substantially amounts to the tracing out of a curve ("critical curve") which shall express the saturation of the solvent C with a mixture in given variable proportions of the other two constituents, A, B; the variation being such that any given point on the curve is related to some other point ("conjugate point") in a way given by the consideration that all mixtures of the three constituents, A, B, C, represented by points lying on the line ("tie-line") joining these two conjugate points ("ideal" alloys, or mixtures), will separate into two different ternary mixtures corresponding with the two points respectively; whereas any mixture of the same constituents, represented by a point lying *outside* the critical curve, will form a "real" alloy, or mixture, not separating spontaneously into two different fluids but existing as a stable homogeneous whole.

The experiments described in Part IV unmistakably point to the conclusion that *whenever sufficiently intimate and prolonged intermixture of the three constituents can be effected, there is no variation whatever* in the position of the point experimentally determined as conjugate to some other given point on the curve, no matter what may be the proportions subsisting between the three constituents employed; but that when metals are used, the practical difficulty in effecting thorough intermixture by stirring when molten is occasionally so great as to lead to slight, but sensible, differences in the composition of the ternary alloys formed simultaneously with some one given alloy approximately conjugate thereto, in different cases where the relative proportions of the constituents are materially different.

A large number of additional experiments on this point have been made, the general result of which is completely to corroborate and

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confirm these conclusions; when the proportions of the constituents are such that approximately equal quantities of the two different ternary alloys are formed, the error due to incomplete intermixture is generally a minimum; this obviously happens when the constituents are used in such proportions as to represent an "ideal" alloy corresponding approximately with the central point of the tie-line uniting the two conjugate points. When, however, the proportions of the constituents differ materially from these, representing an "ideal" alloy considerably nearer to one conjugate point than to the other, so that one of the two ternary alloys is formed in much larger quantity than the other, the effect of incomplete intermixture becomes more marked, more especially when the *heavier* of the two alloys largely preponderates.

In cases where the critical curve is approximately symmetrical with respect to the central line of the triangle drawn from its apex perpendicular to the base, so that the "limiting point" lies near to the apex, the minimum error due to incomplete intermixture is accordingly observed when the two immiscible metals, A, B, are used in approximately equal quantities throughout. If, on the other hand, the critical curve is unsymmetrical, in order to minimise the error due to imperfect intermixture (more especially as regards those parts of the curve where the proportion of the "solvent," C, is greatest), the other two metals, A, B must *not* be used in equal quantity, but the one or the other must be in excess according as the "limiting point" lies on the right or the left-hand side of the central line. Thus, as shown below, in the case of mixtures of chloroform, acetic acid, and water, the limiting point lies considerably to the *left* (chloroform side) of the central line; similarly with mixtures of lead, silver, and zinc, the limiting point is also considerably to the *left* (lead side) of the central line. In such cases the heavier of the two immiscible constituents, A, B (chloroform, lead) must be made to predominate considerably over the lighter one (water, zinc), in order that approximately equal quantities of the two ternary mixtures may be formed. On the other hand, with mixtures of lead (or bismuth), tin, and zinc, the limiting point lies sensibly to the *right* of the central line (zinc side); so that to determine as accurately as possible the positions of the conjugate points situated towards the limiting point, zinc must be made to predominate over lead (or bismuth) in the mixtures employed.

The effect of this in practice is that in order to trace out the critical curve for a given trio of metals the most expeditious way is to begin by preparing two or three mixtures with small quantities of solvent C and approximately equal quantities of A and B; from the results obtained with these mixtures, represented graphically on Stokes' triangular system, a fair idea can generally be formed as to what must be the proportion between A and B, in order to yield with a somewhat larger quantity of C an "ideal" alloy that will separate into approximately equal quantities of the two ternary alloys formed therefrom. Similarly, from these further results, the proportions requisite for the accurate determination of other pairs of conjugate points higher up still can be inferred; and so on. In this way the critical curve is gradually traced out with a much smaller proportion of wasted labour (owing to imperfect formation of truly conjugate ternary alloys) than would otherwise be the case. This method of procedure has accordingly been adopted in the investigation of various critical curves of the kind which will be discussed in a future paper.

These considerations obviously suggest the possibility that, in certain cases at any rate, the mean curve values deduced in the earlier parts of this research may require some little degree of revision, inasmuch as some of the pairs of alloys simultaneously formed were derived from mixtures yielding one alloy in much larger quantity than the other; so that some small amount of experimental error, due to imperfect formation of truly conjugate alloys, might exist. Accordingly, a considerable number of the experiments that might possibly be faulty from this cause have been repeated, using proportions of A and B better suited to the end in view, viz., formation of the two ternary alloys produced in not widely different quantities relatively to one another. Further, a variety of additional experiments have been made with the object of deducing the situations of pairs of conjugate points lying nearer to the limiting points than those previously determined. These further experiments, however, have demonstrated the existence of two other sources of error, not noticeable to so great an extent at the other parts of the critical curve.

In the first place, when an "ideal" alloy is used corresponding with a pair of conjugate points lying near to the limiting point, the two alloys formed differ far less widely in composition than is the case with other pairs more removed from the limiting point; consequently, the densities of the two alloys do not greatly differ, which circumstance appears greatly to impede their complete separation from one another by gravitation whilst standing at rest molten. Secondly, such "ideal" alloys appear to be extremely sensitive to slight differences of temperature, at least as compared with mixtures not so near the limiting point; so that whilst a difference of 10°, 20°, or even 50° C. makes but little difference in the compositions of the two ternary alloys formed from a given "ideal" alloy not near the limiting point, it produces a marked effect on an "ideal" alloy near to that point; in some cases, indeed, a rise of a few degrees in temperature will suffice to transform an "ideal" alloy separating into two ternary alloys considerably different from one another into a "real" alloy not separating at all, but remaining perfectly homogeneous at this slightly higher temperature. Leaving out of sight the practical impossibility of maintaining a lead-bath at 600°—800° C. at an absolutely constant temperature (within, say, ±10°) for eight or ten hours together, the lowering of the temperature taking place on removing the clay test-tube from the lead-bath sometimes appears to cause a measurable amount of separation of a different heavier alloy from the lighter one formed in the bath, and *vice versâ*, during the short time that elapses before the compound mass becomes solid. So that, in fine, duplicate experiments with "ideal" mixtures situated near to the limiting point are apt to yield discordant results owing to one or other of these causes, or to the two combined; and in consequence the direct determination of the exact position of the limiting point is impracticable, although of course its situation can be approximately deduced from the graphical representation of the results on the triangular system. Still nearer approximations can be obtained by the use of other methods kindly suggested by Sir G. G. Stokes, and more fully described below.

The present paper deals with the results of the further experiments made, as above stated, with the mixtures partly described in the previous four Parts* (lead-tin-zinc, bismuth-tin-zinc, lead-silver-zinc, bismuth-silver-zinc, chloroform-acetic acid-water), for the purpose of more completely determining the exact positions of the critical curves for certain definite temperatures, and the systems of tie-lines and their limiting points pertaining to each curve respectively. In a subsequent paper the analogous curves will be described, derived from the combinations of lead or bismuth with zinc as A, B, and cadmium or antimony as C, and with various analogous ternary mixtures where aluminium takes the place of zinc.

Mixtures of Chloroform, Water, and Acetic Acid.

The experiments described in Part IV were continued, using mixtures containing more chloroform than water (from 2 to 3 parts chloroform to 1 of water), and nearly, but not quite, enough acetic acid to form a homogeneous fluid, the composition required being arrived at by adding enough acetic acid to form a single fluid, and then dropping in a little water or chloroform, or both, until separation ensued. With mixtures represented by points lying close to the limiting point, it was found that comparatively slight variations in temperature produced marked alterations in the composition of the two fluids into which the mixture separated, more especially as regards the lighter fluid; thus the same mixture yielded the following figures, according as the temperature at which the mass was maintained during the period of agitation and standing lay near to 20°, 16°, or —4° respectively; whilst at temperatures above 25° a single homogeneous fluid was formed, not separating at all until the temperature was slightly lowered.

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* Part I, 'Roy. Soc. Proc.,' vol. 45, p. 461; Part II, vol. 48, p. 25; Part III, vol. 49, p. 156; Part IV, vol. 49, p. 174.

Temperature.	Heavier fluid.			Lighter fluid.		
	Chloroform.	Water.	Acetic acid.	Chloroform.	Water.	Acetic acid.
20°	55·62	9·60	34·78	30·23	21·89	47·88
16°	56·19	9·56	34·25	26·10	26·04	47·86
−4°	58·88	7·35	33·77	23·00	25·75	51·23

In order to obtain numbers as nearly as possible comparable with one another and with those previously described in Part IV (all of which were obtained at temperatures pretty close to 18°), the mixtures employed were examined at temperatures somewhat above, and also at a little below 18°, in such fashion that the average numbers obtained with each mixture should represent the mean compositions for an average temperature sensibly = 18°. The following average numbers were thus obtained in three such cases:—

No. of tie-line.	Heavier fluid.			Lighter fluid.		
	Chloroform.	Water.	Acetic acid.	Chloroform.	Water.	Acetic acid.
9	67·15	5·20	27·65	18·33	31·11	50·56
10	59·99	7·93	32·08	25·20	25·39	49·41
11	55·81	9·58	34·61	28·85	23·28	47·87

Fig. 1 represents these values, together with those previously described in Part IV, the tie-lines numbered 1 to 8 being those previously described, and those marked 9, 10, and 11, the above three sets of average values respectively. The line *ab* is the tie-line uniting the two points obtained as above-mentioned with one mixture examined at —4° C., obviously belonging to a critical curve lying *outside* the curve for 18°. The point P indicates a mixture of chloro-

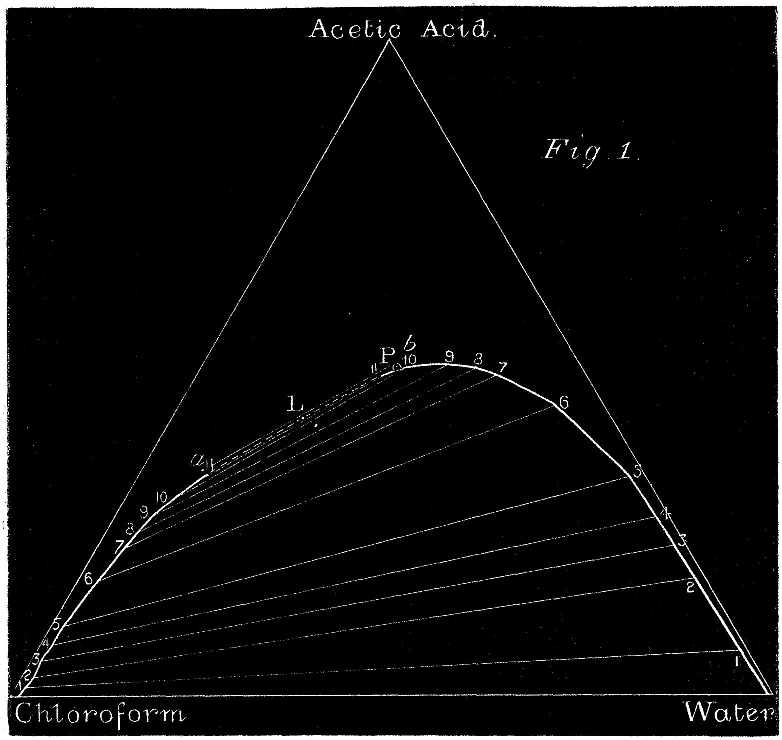


Fig. 1.

form 25 per cent., water 25 per cent., and acetic acid 50 per cent., not separating into two fluids at 18°, as previously described. The point marked L is the "limiting point," deduced from the above figures by means of two different graphical methods suggested by Sir G. G. Stokes.

By the first method, the percentages of chloroform, water, and acetic acid in the heavier liquid being respectively indicated by A, B, and C, and those in the lighter liquid by A′, B′, and C′, the values of A—B (positive quantities) are plotted off as abscissæ to the right, and those of A′—B′ (negative quantities) to the left of the origin, the values of C′—C (positive) being used as ordinates for the first set of abscissæ, and those of C—C′ (negative) for the second set. Fig. 2, curve No. 1, represents the plotting thus obtained; by joining the ends of the two portions of curve thus laid down by the dotted line 11, 11, as shown, a point, *a*, is deduced where this dotted line cuts the base line. This point, *a*, corresponds with the "limiting point," where the lighter and heavier alloys merge into one; when the plotting is carefully made on a sufficiently large scale, the position of

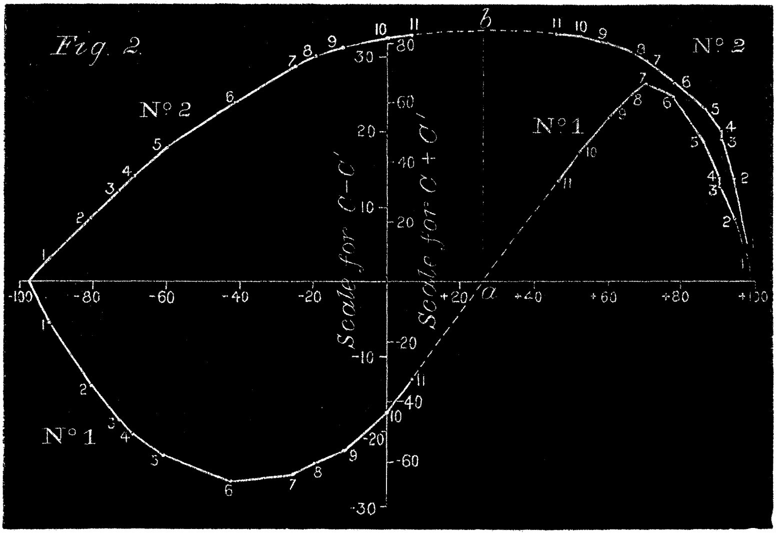


Fig. 2.

a is found to correspond with the value $A-B = 25{\cdot}9$. In similar fashion the values of $C+C'$ are plotted off as ordinates to each of the two sets of abscissæ, and the ends of the two portions of curve No. 2 thus obtained also joined, as shown by this dotted line. A point, b, is thus deduced where this dotted line cuts the perpendicular to the base at the point a. The length ab thus represents the value of $C+C'$ for the point a, *i.e.*, at the "limiting point," when obviously $C = C'$; when the scale is sufficiently large this is found to correspond with the value of $C+C' = 83{\cdot}5$. From these two values for $A-B$ and $C+C'$ ($=2C$), the following values for A, B, and C result:—

$$C = C' = \frac{83{\cdot}5}{2} = 41{\cdot}75$$

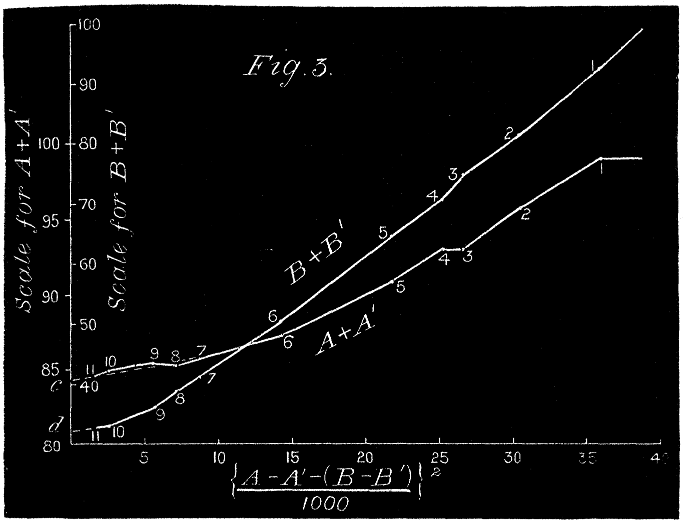
$$\text{whence } A+B = 100-41{\cdot}75 = 58{\cdot}25$$

$$A = \frac{A+B+(A-B)}{2} = \frac{58{\cdot}25+25{\cdot}9}{2} = 42{\cdot}07$$

$$B = \frac{A+B-(A-B)}{2} = \frac{58{\cdot}25-25{\cdot}9}{2} = 16{\cdot}18$$

$$\overline{100{\cdot}00}$$

By the second method. A, B, C, and A′, B′, C′, having tne same meanings as before, two curves are plotted, each with the values of $\{A-A'-(B-B')\}^2$ as abscissæ, one with the values of $A+A'$ as



ordinates, the other with those of $B+B'$. Fig. 3 represents the two curves thus obtained; by prolonging these, as shown by the dotted lines, two points are obtained, *c* and *d*, respectively representing the values of $A+A'$ and $B+B'$, when the abscissa becomes 0, which corresponds with the position of the "limiting point." With a sufficiently large-scale plotting, the points *c* and *d* are found to correspond respectively with the values 84·5 and 32·5; and as at the "limiting point" $A = A'$, and $B = B'$, it thence results that—

$$A = \frac{84{\cdot}5}{2} = 42{\cdot}25$$

$$B = \frac{32{\cdot}5}{2} = 16{\cdot}25$$

$$C = 100-(A+B) = \frac{41{\cdot}50}{100{\cdot}00}$$

The average values for the "limiting point" deduced from the two methods jointly are consequently—

	1st Method.	2nd Method.	Mean.
Chloroform........	42·07	42·25	42·16
Water............	16·18	16·25	16·21
Acetic acid........	41·75	41·50	41·63
	100·00	100·00	100·00

It is noteworthy that the proportion between chloroform and water thus deduced for the "limiting point" is close to that required for the molecular ratio $2CHCl_3$, $5H_2O$.

	Calculated.			Found.		
$2CHCl_3$......	239·0	=	72·64	42·16	=	72·23
$5H_2O$	90·0	=	27·36	16·21	=	27·77
	329·0		100·00	58·37		100·00

But whether this is merely an accidental coincidence, or is really due to a tendency to form a definite hydrate of chloroform in presence of acetic acid, cannot be decided by these experiments alone. The results with alloys subsequently described rather suggest that it is only a coincidence.

Alloys of Lead, Tin, and Zinc.

In Parts I and II seven different series of observations are recorded, made with mixtures of lead, tin, and zinc, at temperatures varying from about 565° C. up to near 800°, and containing lead and zinc in ratios varying from 2 : 1 to 1 : 2. On plotting these different series on the triangular system, it is evident that the critical curves deduced from those experiments where the temperature did not exceed 689—750° are substantially identical, whereas that derived from experiments at a higher temperature, 750—850° averaging near 800°, lies perceptibly *inside* the others. Again, but little discordance between the general directions and degrees of slope of the tie-lines is noticed in any of the series at temperatures not above 750° where the ratio of lead to zinc was 1 : 1 or 1 : 2; with the series where this ratio was 2 : 1, however, the upper ties do not closely coincide with those derived from the other series, but (as pointed out by Sir G. G. Stokes, Part IV) are inclined to them at angles not far from 5°, thus indicating the existence of some cause constantly at work interfering with separation into truly conjugate alloys; obviously this cause is the large preponderance of heavier alloy formed over lighter alloy, which, as above stated, produces a marked effect on the result by preventing thorough intermixture by stirring.

On plotting out in these seven cases the values of $\{A-A'-(B-B')\}^2$ as abscissæ, and of $A+A'$ and $B+B'$ as ordinates (Stokes' 2nd method, *supra*), similar differences are observed. All the experiments at 565—750° concord fairly well when the series where the ratio of lead to zinc was 1 : 1 or 1 : 2 are taken into account; whereas the series where the ratio was 2 : 1 exhibit a much wider departure. The experiments at 750—850°, and the concordant ones at 565—750°

lead to the following approximations respectively to the composition of the mixtures of metals at the limiting point:—

	565—750°		750—850°	
Lead......	21—23;	say 22	23—25;	say 24
Tin.......	34—36	„ 35	31—33	„ 32
Zinc......	42—44	„ 43	43—45	„ 44
		100		100

The critical curve for the higher temperature consequently lies *inside* that for the lower temperature, since it contains a limiting point corresponding with a smaller tin percentage.

In order to define the upper portion of the critical curve still more exactly, and thus to deduce a closer approximation to the true limiting point, a number of additional experiments were made at a temperature close to 650°, with mixtures containing 31 to 34 per cent. of tin, and lead and zinc in proportions lying between 1 : 1·75 and 1 : 2, this being the ratio calculated to yield approximately equal quantities of heavier and lighter alloys, and thus to minimise the error due to imperfect intermixture. The following table gives the average values finally deduced from these experiments, together with the majority of the valuations derived from Series I, II, III, IV, and V (Part I), a few experiments in these series being discarded, together

No. tie-line.	Heavier alloy.			Lighter alloy.			Excess of tin percentage in lighter alloy over that in heavier.
	Tin.	Zinc.	Lead.	Tin.	Zinc.	Lead.	
—	0	1·24	98·76	0	98·86	1·14	—
1	4·45	1·76	93·79	6·64	90·75	2·61	+2·19
2	6·94	2·05	91·01	9·91	86·71	3·38	+2·97
3	9·60	2·49	87·91	13·47	82·18	4·35	+3·87
4	12·60	3·66	83·74	16·68	78·48	4·84	+4·08
5	14·76	4·22	81·02	19·27	75·36	5·37	+4·51
6	16·11	4·73	79·16	20·35	73·51	6·14	+4·24
7	18·71	5·62	75·67	22·51	70·04	7·45	+3·80
8	21·95	7·57	70·48	25·07	66·72	8·21	+3·12
9	26·28	13·24	60·48	27·49	62·33	10·18	+1·21
10	29·43	16·76	53·81	28·64	59·94	11·42	−0·79
11	31·63	19·73	48·64	29·58	57·87	12·55	−2·05
12	33·88	22·36	43·76	30·33	56·25	13·42	−3·58
13	35·03	25·38	39·59	30·24	55·33	14·43	−4·79
14	35·65	35·25	29·10	32·85	48·51	18·64	−2·80

with the entire Series VI where excess of lead was used, on account of showing less general concordance with the average than the others, obviously on account of incomplete intermixture and consequent formation of alloys not so truly conjugate as in the other cases. In all 88 compound ingots, and consequently 176 ternary alloys, were used in the deduction of the 14 pairs of conjugate points thus tabulated, so that each point represents the average of somewhat more than six alloy analyses.

Fig. 4 represents these values plotted on the triangular system.

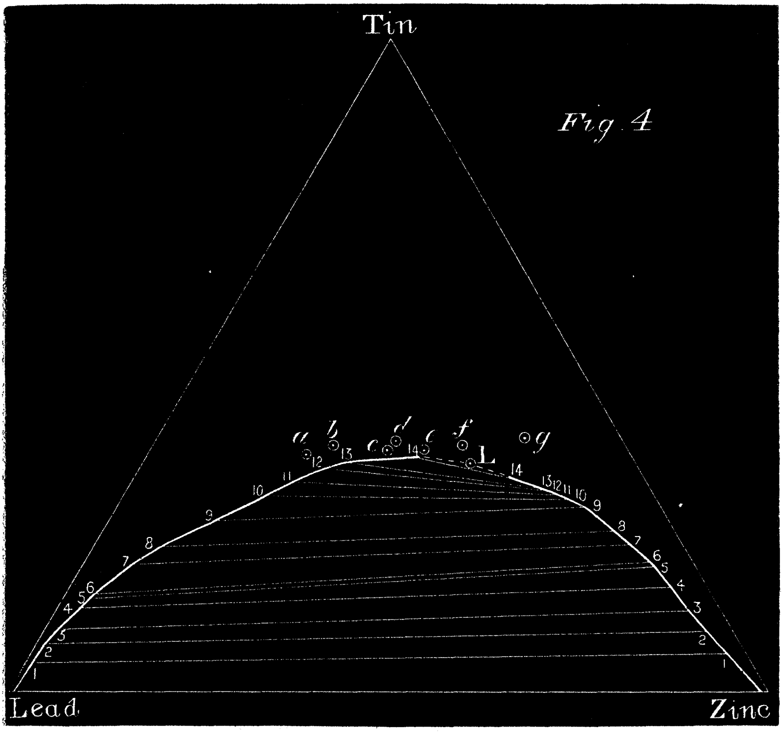


Fig. 4

On comparing the figures in the last column with the corresponding ones obtained in the previous experiments (Part I), it is noticeable that the tin distribution is such that the excess of tin percentage in the lighter alloy over that in the heavier one now shows *two* maxima, the second of which was not indicated by the former less complete series. The first is a + maximum, arrived at near the 5th tie-line; the second a — maximum, situated near to the 13th. Obviously the existence of a maximum (+ or —) is a necessary result of a slope of the tie-lines to the one side or the other, since the lowest possible tie unites the points obtained with a percentage of solvent metal = *nil*, whilst the upper ties dwindle down to a point at the limiting point, so that for each of these limiting ties the percentage of solvent metal is the same in both heavier and lighter alloy formed; but it is noticeable that only in one other case out of a dozen ternary alloys now under examination is a *second* maximum noticeable, *i.e.*, only in this one other case (lead-aluminium-tin alloys) are the upper and lower ties found to slope in opposite directions; in all other instances, whether the ties slope to the right or to the left, the direction of the slope is the same throughout the whole extent of the critical curve.

It is further noticeable that both with lead-zinc-tin and lead-aluminium-tin alloys the position of the first maximum is such that it occurs when the ratio of lead to tin in the heavier alloy is sensibly near to that indicated by the formula $SnPb_3$. Thus in the case of the lead-zinc-tin alloys above described—

	Calculated.		Found.	
Sn	118 =	15·97	14·76 =	15·41
Pb_3	621 =	84·03	81·02 =	84·59
	739 =	100·00	95·78 =	100·00

The parallel results obtained with lead-aluminium-tin alloys will be described in a future paper; it may be noticed, however, that with neither series of alloys is any marked elevation or depression in the outline of the critical curve noticeable at the part corresponding with the compound $SnPb_3$, unlike the curve obtained with lead-zinc-silver and bismuth-sinc-silver alloys, where the formation of the definite compounds $AgZn_5$ and Ag_4Zn_5 leads to marked alterations of outline (*vide infra*).

It was found impracticable to obtain any accurate valuations of tie-lines situated nearer to the limiting point than No. 14; several attempts were made, but the results exhibited too great an amount of discordance amongst themselves, and too wide departures from the curve indicated by the above experiments, to enable them to be regarded as trustworthy; the causes of this being, as above stated, the slight difference in density between the two alloys formed, and the relatively large effect of temperature variation at this part of the curve as compared with other portions further removed from the limiting point. In fig. 4 (representing the above table plotted on the triangular system) L is the limiting point deduced by Stokes' 2nd Method from a carefully made large-scale plotting, giving as the most probable values $A+A' = 45$ and $B+B' = 85$, whence

$$\begin{array}{lcccr} \text{Lead} & = & \frac{45}{2} & = & 22{\cdot}5 \\ \text{Zinc} & = & \frac{85}{2} & = & 42{\cdot}5 \\ \text{Tin} & = & & & 35{\cdot}0 \\ \hline & & & & 100{\cdot}0 \end{array}$$

On account of the peculiar serpentine form of the curve obtained by the 1st Method, the positions of the limiting point cannot be so readily deduced by this method as in the case of chloroform, acetic acid, and water.

The points marked *a*, *b*, *c*, *d*, *e*, *f*, *g*, respectively indicate various "real" alloys obtained in the course of the experiments described in Parts I and II.

Critical Curve at 800°.

The experiments at temperatures lying between 750° and 850°, detailed in Part II, were similarly supplemented by some additional ones made with mixtures containing lead and zinc in the proportion 1 : 1·75 to 1 : 2, so as to obtain more accurate valuations, more especially in the case of the pairs of conjugate points lying nearer to the limiting point. The following table represents the average values finally obtained from these additional valuations conjointly with the former ones.

No. of tie-line.	Heavier alloy.			Lighter alloy.		
	Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.
—	0	98·70	1·30	0	1·57	98·43
1	6·51	89·97	3·52	9·56	4·20	86·24
2	12·04	83·09	4·87	15·80	7·13	77·07
3	16·31	78·17	5·52	19·84	8·87	71·29
4	18·81	74·02	7·17	21·79	10·64	67·57
5	21·29	69·12	9·59	23·80	10·60	65·60
6	24·60	61·77	13·63	25·33	12·30	62·37
7	26·43	57·07	16·50	26·44	12·15	61·41
8	29·12	50·51	20·37	28·47	12·64	58·89

Fig. 5 represents these values, the exterior curve indicating the numbers above stated for temperatures near to 650°. The points marked A and B represent two mixtures examined, not separating into two at 800°, although lying inside the critical curve for 650°.

On applying Stokes' 2nd Method, the curves marked No. 1, fig. 6, are obtained, those marked No. 2 being the corresponding curves deduced from the mean values at 650° above described. Obviously

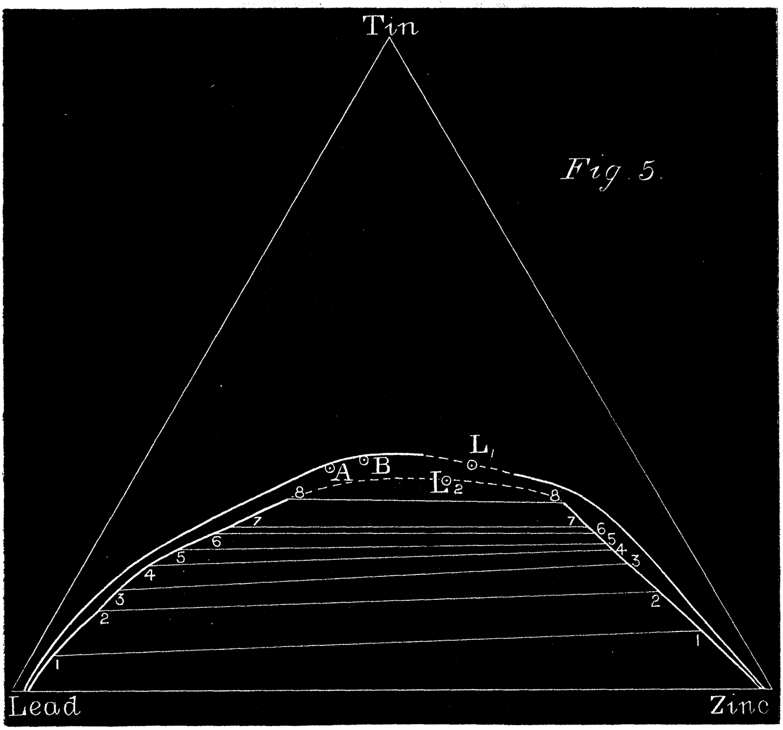
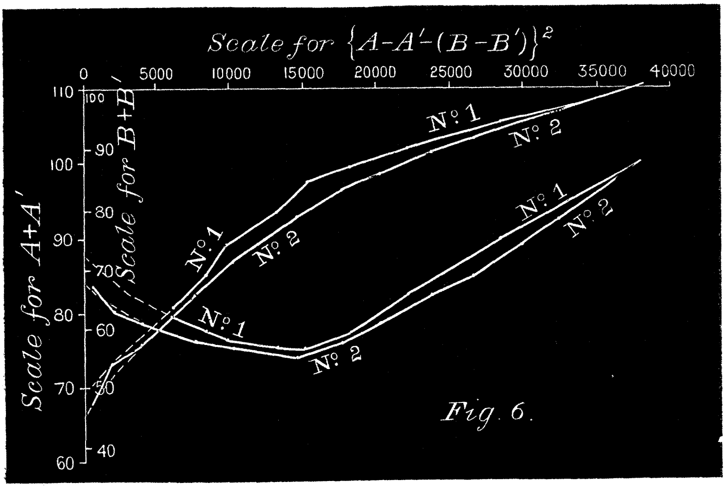

Tin
L₁
A
B
L₂
8
7
6
5
4
3
2
1
Lead
Zinc

Fig. 5.


Scale for $\{A-A'-(B-B')\}^2$
0
5000
10000
15000
20000
25000
30000
35000
40000
Scale for A+A′
110
100
90
80
70
60
Scale for B+B′
100
90
80
70
60
50
40
N° 1
N° 2
N° 1
N° 2
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N° 2
N° 1
N° 2

Fig. 6.

the curves marked 1 are closely in accordance with those deducible by shifting the curves marked 2 upwards on the paper; so that it may fairly be inferred that whilst the values of A+A′ and B+B′ at the limiting point are close to 45 and 85 respectively, those for curves No. 2 are not far from A+A′ = 48, and B+B′ = 88, as indicated by the dotted prolongations: whence, the compositions at this limiting point for 650° C. and 800° C. respectively are close to

	At 650°.	At 800°.
Lead	22·5	24·0
Zinc	42·5	44·0
Tin..........	35·0	32·0
	100·0	100·0

The points marked L_1 and L_2 (fig. 5) respectively indicate these compositions.

It is worthy of notice that in each case the ratio between lead and zinc is not far from that indicated by the formula $PbZn_6$.

	Calculated.	Found. At 650°.			Found. At 800°.		
Lead ..	34·67	22·5	=	34·62	24·0	=	35·29
Zinc ..	65·33	42·5	=	65·38	44·0	=	64·71
	100·00	65·0		100·00	68·0		100·00

A priori, it would seem not impossible that the position of the limiting point might correspond with the formation of a definite compound of the two immiscible metals, soluble in the "solvent" metal to an extent varying with the temperature. On the other hand, the experiments subsequently described show that when silver replaces tin as solvent metal an entirely different ratio between lead and zinc subsists at the limiting point thus found, more nearly approximating to Pb_2Zn. Experiments now in progress, moreover, indicate that with antimony as solvent metal a third ratio, approximately $PbZn_2$, is deduced.

It is further noticeable that the upper tie-lines, depicted in fig. 4 (Nos. 9 to 14), visibly converge together in such fashion that the point representing the composition Sn = 28, Pb = 11, Zn = 61 per cent. lies in the midst of them all. This configuration obviously suggests that there is a tendency to the formation of some definite compound, such that whilst a considerable range in composition is shown by the heavier alloys, a much smaller one is observed in the case of the lighter alloys conjugate therewith; that this compound is indicated by the formula $SnZn_4$ is strongly suggested by the circumstance that in this compound the two metals are to one another nearly in the ratio of that existing at this central point—

	Calculated for $SnZn_4$.	Found.		
Tin..........	31·2	28	=	31·5
Zinc.........	68·8	61	=	68·5
	100·0	89		100·0

It will be shown in a future paper, that analogous convergent dispositions of the lines are observed with other ternary metallic mixtures, also leading to the conclusion that definite compounds are formed; a well marked case in point is noticed with alloys of lead, zinc, and cadmium, where a marked convergence is observable to a point where the cadmium and lead are in the ratio indicated by the formula $CdPb_2$.

Alloys of Bismuth, Tin, and Zinc.

The experiments described in Part III, when plotted on the triangular system, indicate that the limiting point in the critical curve for mixtures of bismuth, tin, and zinc is situated to the *right* (zinc side) of the central line of the triangle; so that in order to determine, with the least amount of error through imperfect intermixture, the conjugate points situated near the limiting point, the mixtures used must contain more zinc than bismuth. Accordingly a number of additional experiments were made with mixtures containing bismuth and zinc in the proportion 1 : 2·5 to 1 : 3·5, and from 12 to 21 per cent. of tin. The figures thus obtained showed that some of the compound ingots previously examined (prepared with equal quantities of bismuth and zinc) were slightly but sensibly affected by the error due to incomplete intermixture, owing to the preponderance of heavier alloy formed over the lighter one. The following table exhibits the average values finally deduced from these further experiments, together with those of the former series not materially affected by this source of error, at temperatures averaging near to 650° C. It is noticeable that these further experiments show that the numerical value of the excess of tin percentage in the lighter alloy over that in the heavier attains a maximum (of negative sign), and then diminishes again; a point not shown by the less complete series of values described in Part III.

Fig. 7, curve No. 1, represents these values, No. 2 representing the analogous figures obtained at 700°—800° (Series II, Part III). Obviously the critical curve for the higher temperature lies *inside* that for the lower temperature, as in the case of the lead-zinc-tin alloys above described. The point marked A represents a mixture not sepa-

No. of tie-line.	Heavier alloy.			Lighter alloy.			Excess of tin percentage in lighter alloy over that in heavier.
	Tin.	Bismuth.	Zinc.	Tin.	Bismuth.	Zinc.	
—	0	85·72	14·28	0	2·32	97·68	0
1	3·23	80·27	16·50	1·98	3·45	94·57	−1·25
2	6·35	75·82	17·83	3·97	4·21	91·82	−2·38
3	10·38	70·52	19·10	6·35	5·53	88·12	−4·03
4	13·53	66·33	20·14	7·95	6·51	85·54	−5·58
5	19·09	51·35	29·56	11·19	8·68	80·13	−7·90
6	20·80	46·01	33·19	12·72	9·72	77·56	−8·08
7	20·44	42·43	37·13	12·98	9·70	77·32	−7·46
8	21·89	30·33	47·78	17·25	11·92	70·83	−4·64
9	22·37	25·94	51·69	19·16	13·04	67·80	−3·21

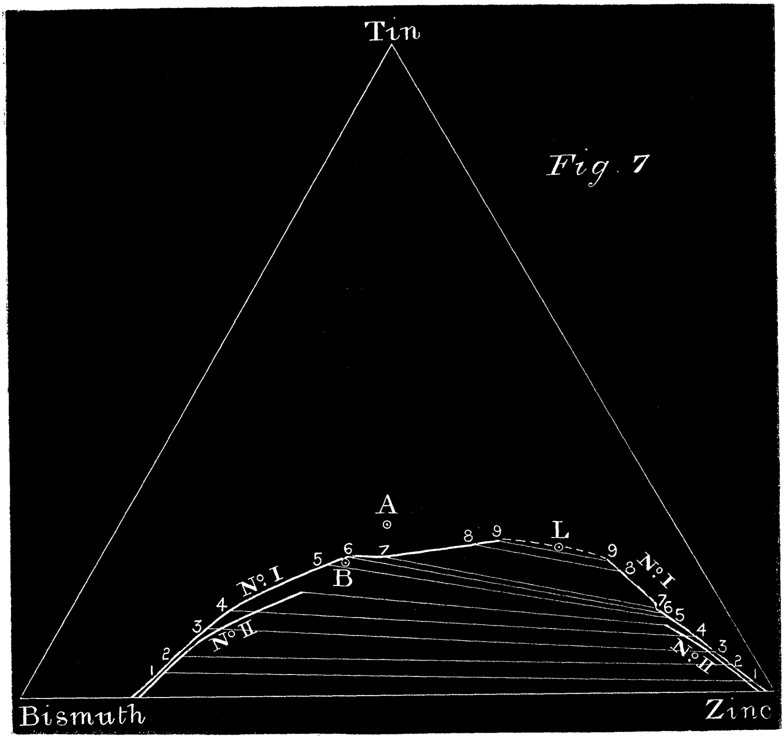


Fig. 7

rating into two at 650° ("real" alloy); that marked B, a similar mixture, not separating at 750°; these contained respectively (average of analyses of both ends) :—

	A.	B.
Bismuth	38·7	48·2
Zinc	35·3	31·8
Tin	26·0	20·0
	100·0	100·0

The point B evidently falls well outside the critical curve for 750°, although it is not distinctly outside that for 650°.

On applying Stokes' second system to the above values, the following figures result from a large-scale plotting:—$A+A' = 37$, $B+B' = 120$; whence the composition for the limiting point, L, is:—

Bismuth	18·5
Zinc	60·0
Tin	21·5
	100·0

These percentages of bismuth and zinc are not far from those required for the formula $BiZn_{10}$.

	Calculated.	Found.		
Bismuth	24·4	18·5	=	23·5
Zinc	75·6	60·0	=	76·5
	100·0			100·0

Inasmuch, however, as an entirely different proportion is found when silver is the "solvent" metal (approximately $BiZn_2$), this cannot be regarded as much evidence of the existence of an atomic compound of bismuth and zinc at the limiting point.

On contrasting together the curves thus deduced for mixtures of lead-zinc-tin and bismuth-zinc-tin, it is obvious that in each case the curve for a higher temperature lies *inside* that for a lower temperature. When bismuth is the heavier immiscible metal, the curve lies inside that obtained with lead instead of bismuth; apparently the same relationship holds in the case of $\left.\begin{matrix}\text{bismuth}\\\text{lead}\end{matrix}\right\}$-zinc-silver alloys and of $\left.\begin{matrix}\text{bismuth}\\\text{lead}\end{matrix}\right\}$-aluminium-tin alloys, as will be hereafter discussed.

The limiting points above deduced in each case lie to the *right* (zinc side) of the central line of the triangle, and the uppermost tie-lines in each case slope to the right. With bismuth-zinc-tin alloys the same disposition is also observed with the lower tie-lines, but with lead-zinc-tin alloys the lower ties slope to the left, the reason for this difference probably being that lead and tin exhibit a tendency to combine together to form a definite compound, $SnPb_3$, the formation of which affects the composition of certain of the heavier alloys, whilst no similar compound appears to be formed between bismuth and tin. Owing to the critical curve for bismuth-zinc-tin being so much lower down than that for lead-zinc-tin, the tendency towards formation of the compound $SnZn_4$, which affects the direction of slope of the ties in the latter curve, is almost invisible with the former ones. Some slight indication of an effect is, however, perceptible, the slope of the ties to the right visibly ceasing to increase towards the upper part of the curve in the same marked way as is noticeable at the lower part thereof. It is remarkable in this connexion that the upper ties with alloys of lead and zinc, when tin is the solvent metal, are the only ones sloping downwards to the right, those obtained with lead and zinc when silver, cadmium, or antimony is the solvent metal, uniformly sloping downwards to the left. Precisely the same remarks apply to the corresponding alloys containing aluminium instead of zinc so far as at present examined.

Alloys of Lead, Silver, and Zinc.

The experiments detailed in Part II indicate that the position of the limiting point with lead-silver-zinc alloys lies considerably to the *left* of the central line of the triangle, and not to the right as with the above-described alloys containing tin. Accordingly, a number of additional experiments were made with mixtures containing lead and zinc in proportions from 3 : 2 to 4 : 1 (according to the amount of silver present), with the object of correcting any possibly erroneous values due to imperfect intermixture owing to inequality between the quantities of heavier and lighter alloys formed; and also of obtaining pairs of conjugate points situated nearer to the limiting point than those already deduced, and thus of enabling the position of the limiting point itself to be calculated. In all these further experiments the percentage of silver in the mixture exceeded 20, so that only those points were re-valued lying nearer to the limiting point than those where the effect of the formation of the compound $AgZn_5$ in producing irregularity became appreciable. The temperature was 750°—850° throughout, averaging near to 800° as before.

The following table represents the average results obtained by taking into consideration these further experiments, together with those described in Series I and II, Part II, none of which were found to be affected by the error due to incomplete intermixture to anything like so great an extent as was found with some few of the ingots prepared with tin. The 14 pairs of conjugate points are deduced from the examination of 39 compound ingots in all, representing 78 ternary alloys. Each point, therefore, nearly represents the average of three alloy analyses.

No. of tie-line.	Heavier alloy.			Lighter alloy.		
	Silver.	Lead.	Zinc.	Silver.	Lead.	Zinc.
1	1·25	96·69	2·06	38·91	3·12	57·97
2	1·54	96·28	2·18	40·89	3·38	55·73
3	1·71	96·43	1·86	45·01	3·37	51·62
4	2·39	95·78	1·83	47·68	3·74	48·58
5	4·18	94·43	1·39	52·80	4·09	43·11
6	5·55	93·16	1·29	54·93	4·21	40·86
7	10·22	88·02	1·76	60·14	9·00	30·86
8	12·62	85·38	2·00	63·70	11·30	25·00
9	15·69	81·88	2·43	65·34	13·87	20·79
10	17·43	80·15	2·42	65·94	14·79	19·27
11	17·65	79·78	2·57	67·03	16·48	16·49
12	19·51	78·54	1·95	63·79	22·29	13·92
13	29·53	68·03	2·44	60·35	28·42	11·23
14	29·90	67·21	2·89	59·32	29·15	11·53

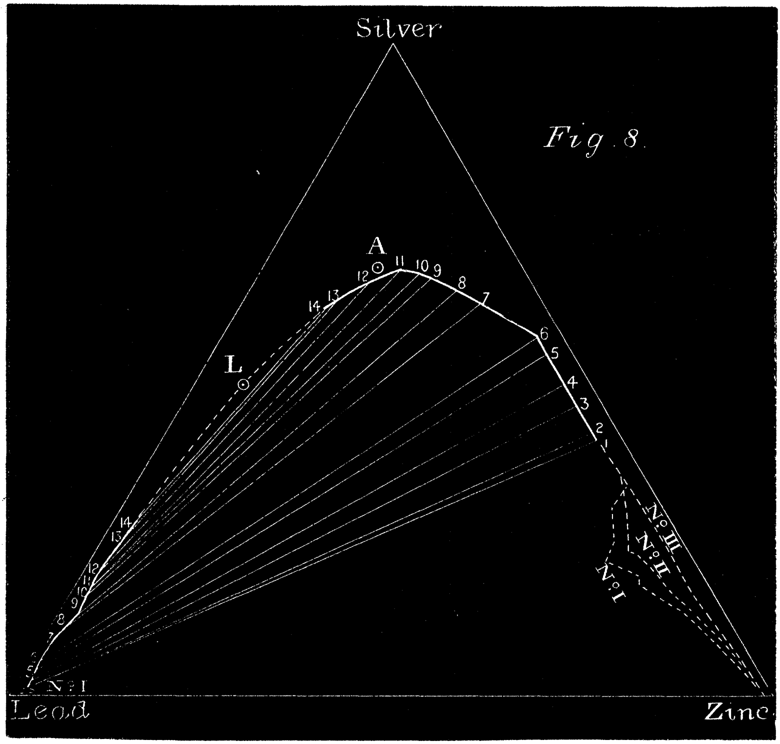


Fig. 8.

Fig. 8 represents these values on the triangular system, the point A indicating an alloy that did not separate, containing Ag = 67·5, Pb = 20·1, Zn = 12·4.

The position of the limiting point L is found by a large-scale plotting on Stokes' second system to correspond with the values :—

$$A + A' = 96{\cdot}4$$

$$B + B' = 12{\cdot}6$$

whence the composition at the limiting point is :—

Lead = 48·2
Zinc = 6·3
Silver = 45·5
100·0

It is noteworthy that the ratio between lead and zinc at the limiting point thus found with silver as the "solvent" metal, is entirely different from that deduced above when tin is the solvent; with tin, the ratio corresponds pretty closely with that indicated by the formula $PbZn_6$, whereas with silver it corresponds more nearly with Pb_2Zn.

	Calculated.	Found.		
Pb..........	86·43	48·2	=	88·44
Zn..........	13·57	6·3	=	11·56
	100·00	54·5		100·00

The dotted lines I, II, III at the lower portions of the critical curve represent the values described in Series I, II, and III respectively (Part II), and indicate very clearly the effect produced by the formation of the definite compound $AgZn_5$, and its gradual elimination as previously described. Similarly, the effect of the formation of the compound Ag_4Zn_5 is readily visible in the right-hand branch of the curve; the conjugate point No. 6 is obviously close to an angle in the curve line and represents an alloy containing silver and zinc in the proportions 54·93 and 41·86, or almost exactly Ag_4Zn_5.

	Calculated.	Observed.		
Silver......	57·07	54·93	=	56·75
Lead.......	42·93	41·86	=	43·25
	100·00	96·79		100·00

Leaving out of sight the bulge inwards at the lower part of the curve, due to the formation of $AgZn_5$, it is noticeable that the critical curve for lead and zinc with silver as "solvent" metal lies *outside* that with tin as solvent. As shown below, the same relationship also holds with bismuth-zinc-silver and bismuth-zinc-tin curves.

Alloys of Bismuth, Silver, and Zinc.

The experiments described in Part III show that with bismuth-zinc-silver alloys, as with those of lead-zinc-silver, the position of the limiting point lies to the *left* (bismuth side) of the central line. Accordingly, a number of additional experiments were made with silver percentages upwards of twenty, and with zinc and bismuth in the proportions 1 : 1·33 to 1 : 1·5, so as to deduce more accurately and completely the upper portion of the critical curve, only those points being re-valued where the influence of the formation of the compound $AgZn_5$ had become inappreciable.

The following table exhibits the average results thus obtained, together with those described in Series I (Part II), the temperature throughout being 700°—800°, averaging near to 750°; twenty-four compound ingots in all being employed, representing forty-eight ternary alloys.

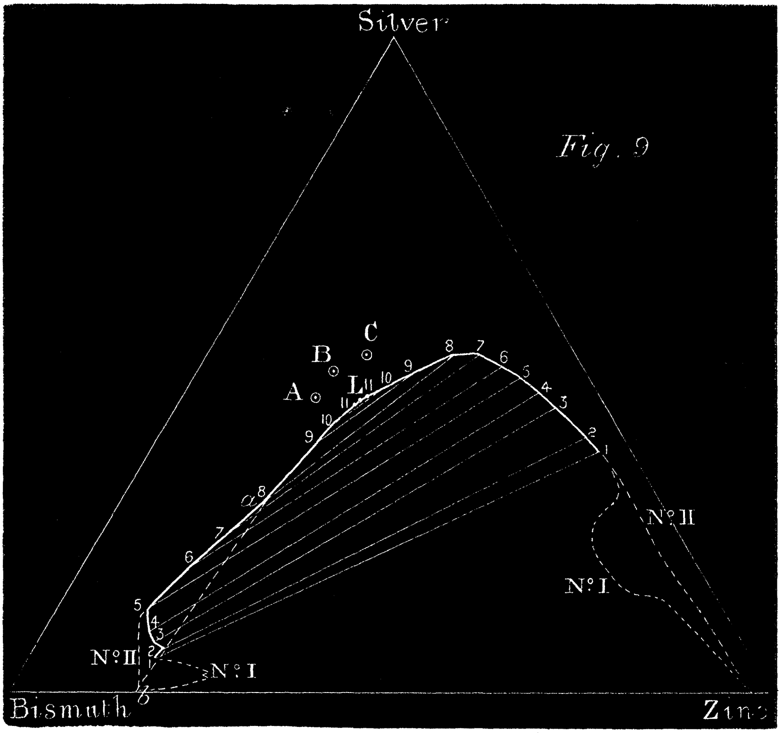
No. of tie-line.	Heavier alloy.			Lighter alloy.		
	Silver.	Bismuth.	Zinc.	Silver.	Bismuth.	Zinc.
1	5·08	79·28	15·64	37·06	5·34	57·60
2	6·84	77·24	15·92	38·80	5·93	55·27
3	7·58	78·58	13·84	43·16	7·99	48·85
4	8·98	77·99	13·03	46·31	8·67	45·02
5	12·71	76·19	11·10	47·94	10·05	42·01
6	18·68	68·97	12·35	49·92	12·42	37·66
7	22·96	62·72	14·32	51·34	14·34	34·32
8	29·26	53·10	17·64	51·16	17·21	31·63
9	37·33	43·27	19·40	49·73	22·78	27·49
10	41·22	38·52	20·26	47·15	28·76	24·09
11	43·74	33·82	22·44	45·25	32·11	22·64

Fig. 9 represents these results on the triangular system, the position of the limiting point L being thence deduced by Stokes' second system, a large-scale plotting giving the values :—

$$A + A' = 66{\cdot}25$$

$$B + B' = 44{\cdot}5$$

whence the composition at the limiting point is :—



Bismuth.........	33·12
Zinc.............	22·25
Silver...........	44·63
	100·00

This represents a ratio between bismuth and zinc not far from that indicated by the formula $BiZn_2$; whereas the corresponding ratio with tin as solvent metal was found to be not far from that indicated by $BiZn_{10}$.

	Calculated.	Found.		
Bismuth....	61·76	33·12	=	59·82
Zinc	38·24	22·25	=	40·18
	100·00	55·37		100·00

The dotted lines I and II at the base of the critical curve represent respectively the values given in Series I (Part III), obtained by fusion for eight hours, and in Series II and III, obtained by separate further fusion of the lighter and heavier alloys thus formed. Like the corresponding results obtained with lead-zinc-silver alloys shown in fig. 8, these lines clearly indicate the effects due to the formation of $AgZn_5$ and Ag_4Zn_5; the formation of the first leading to a marked bulge *inwards* on both sides of the curve at the lowest part; and that of the second to an *outward* bulge somewhat higher up in the left-hand branch, as compared with the dotted line *ab* connecting the upper part of the curve with the point *b* on the base line, representing the alloy of bismuth and zinc formed in the absence of "solvent" metal.

The points marked A, B, and C represent certain mixtures examined that did not separate into two different alloys, *i.e.*, that formed "real" alloys at 750°.

Leaving out of sight the lower bulges inwards and outwards, due to formation of $AgZn_5$ and Ag_4Zn_5, it is evident that the critical curve for bismuth-zinc-silver lies *inside* that for lead-zinc-silver, just as that for bismuth-zinc-tin lies inside that for lead-zinc-tin. Further, the curve for bismuth-zinc-silver lies *outside* that for bismuth-zinc-tin just as the curve for lead-zinc-silver lies outside that for lead-zinc-tin. With silver as "solvent" metal the limiting point lies to the *left* of the central line of the triangle (bismuth or lead side); whilst with tin as solvent metal it lies to the right (zinc side). In the first case the ties uniformly slope downwards to the left, and in the second, to the right so far as the upper ones are concerned; although a slope to the left is observed with the lower ones for the lead-zinc-tin alloys, suggesting the existence of a tendency to form a definite compound of lead and tin (possibly $SnPb_3$), no analogous tendency being noticeable with bismuth and tin.

The author has much pleasure in acknowledging the assistance afforded him by Mr. Sydney Joyce in carrying out the further experiments above described.

IV. "Note on some Specimens of Rock which have been exposed to High Temperatures." By Professor T. G. BONNEY, D.Sc., LL.D., F.R.S. Received December 18, 1891.

The effects of raising several varieties of rock to temperatures which, though high, in some cases were below those required to produce fusion were described to the Royal Society by Mr. Rutley in 1886.* The following notes may be useful as a continuation of a subject which is not without interest owing to its bearing on natural processes.

Some time since, Mr. J. Postlethwaite, F.G.S., of Keswick, kindly

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* 'Roy. Soc. Proc.,' vol. 40, p. 430.

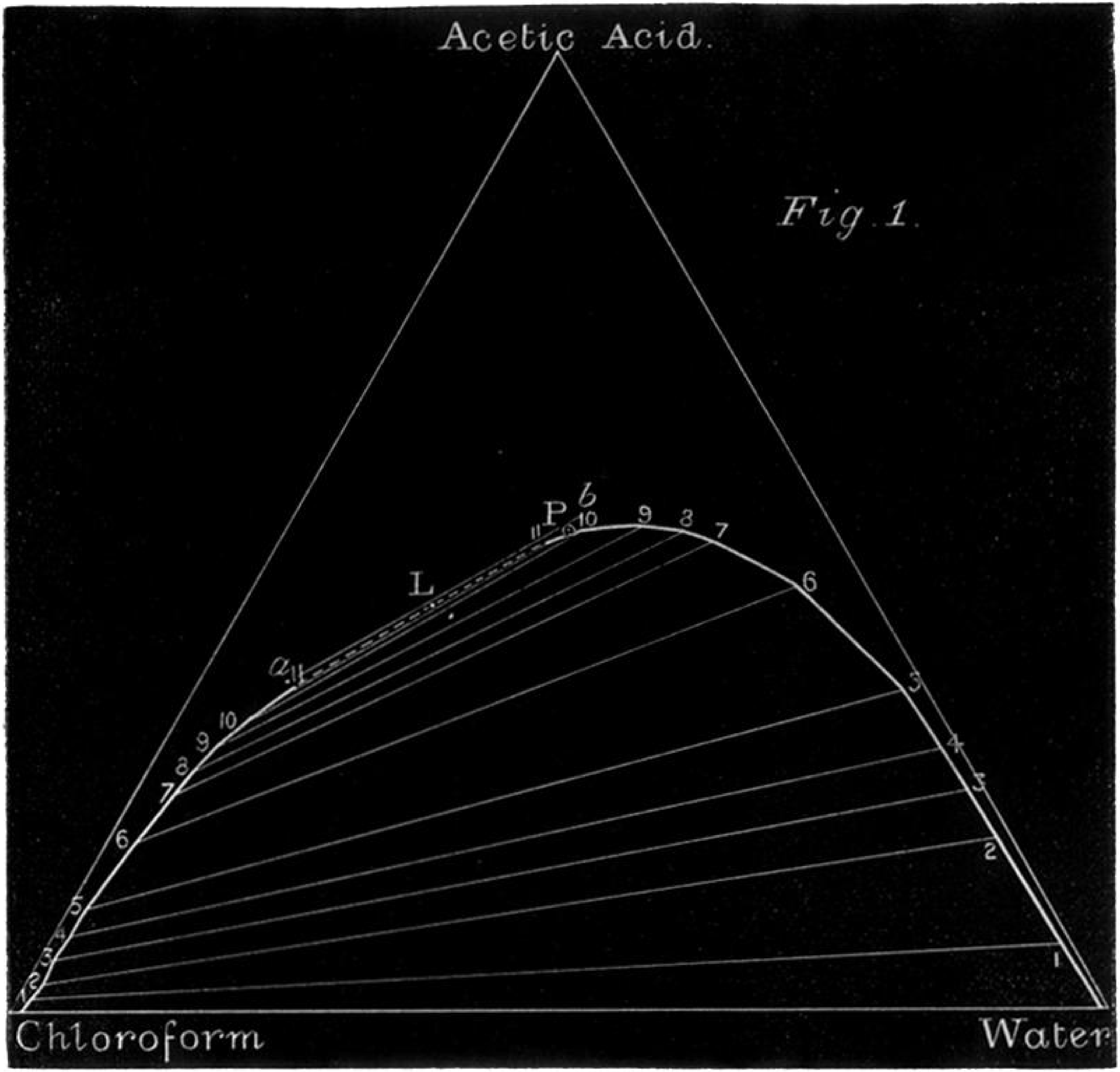


Fig. 1.

Acetic Acid.
Chloroform
Water
P
b
L
a
1
2
3
4
5
6
7
8
9
10
11
1
2
3
4
5
6
7
8
9
10
11

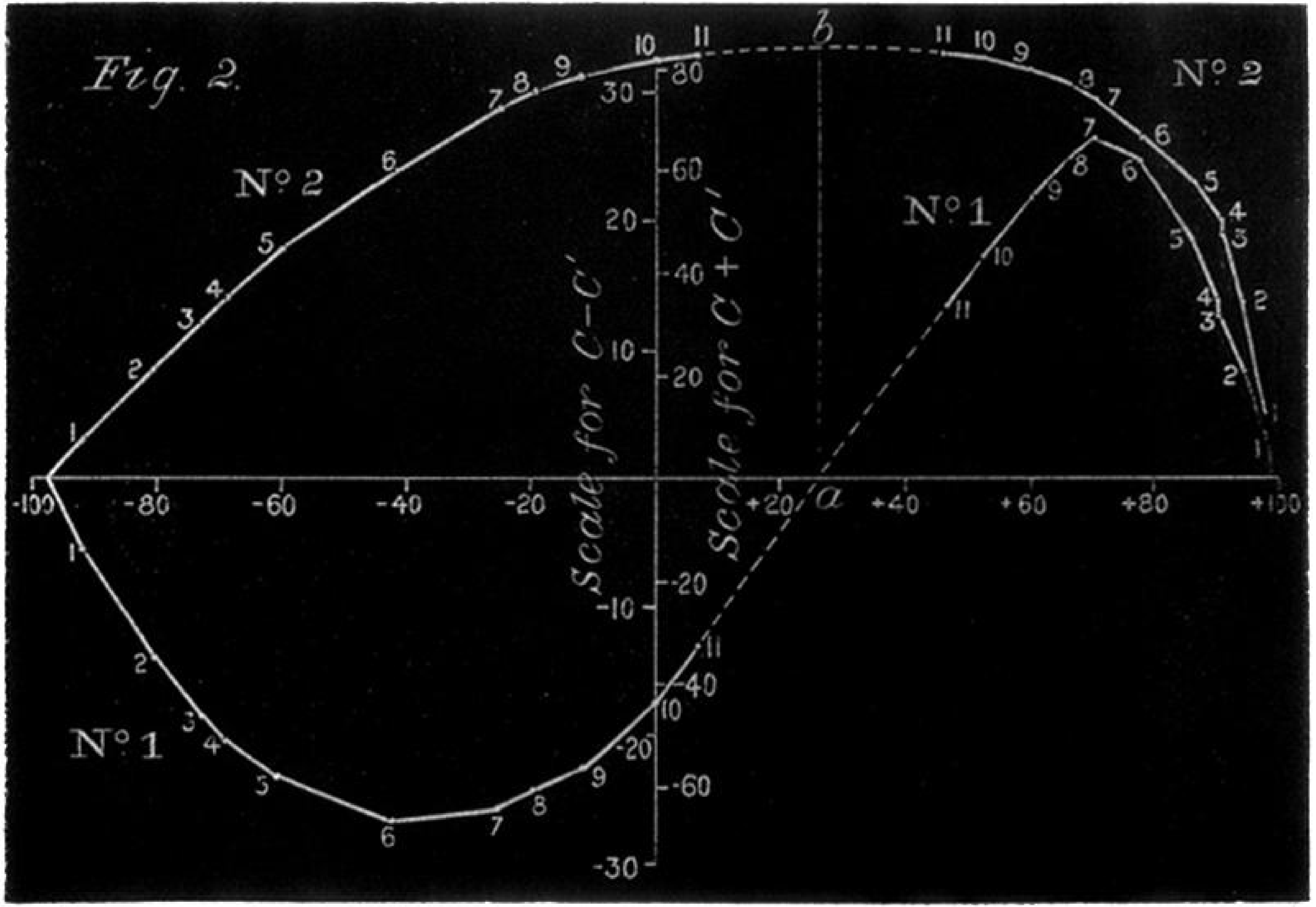
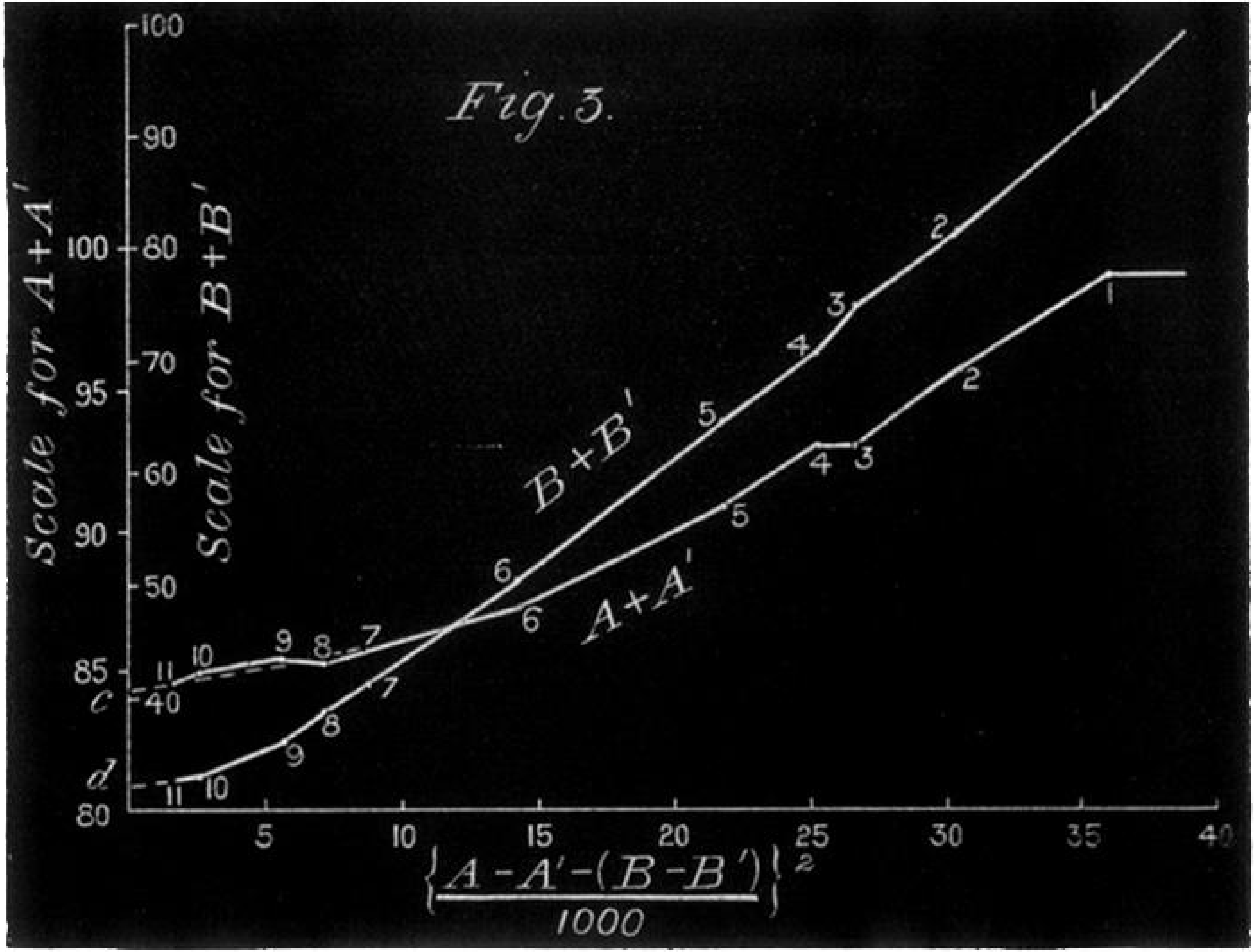


Fig. 2.

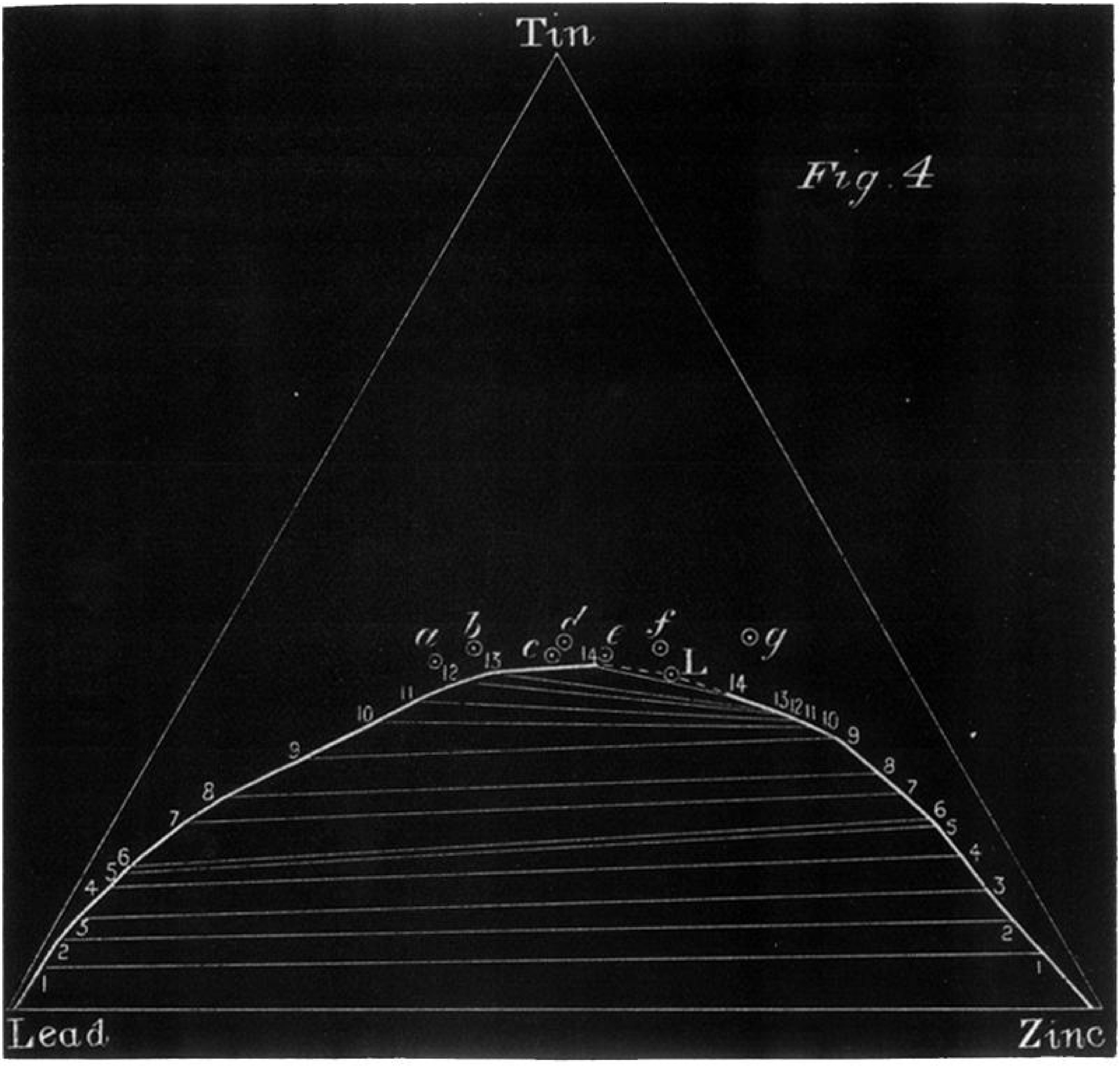
No. 2
No. 1
No. 2
No. 1
b
a
Scale for C−C′
Scale for C+C′
30
20
10
-10
-30
80
60
40
20
-20
-40
-20
-60
-100
-80
-60
-40
-20
+20
+40
+60
+80
+100
1
2
3
4
5
6
7
8
9
10
11

Fig. 3.



Scale for A+A'
Scale for B+B'
100
90
80
70
60
50
40
100
95
90
85
80
c
d
B+B'
A+A'
1
2
3
4
5
6
7
8
9
10
11
5
10
15
20
25
30
35
40
$\left\{\frac{A-A'-(B-B')}{1000}\right\}^2$

Fig. 4


Tin
Lead
Zinc
a
b
c
d
e
f
g
L

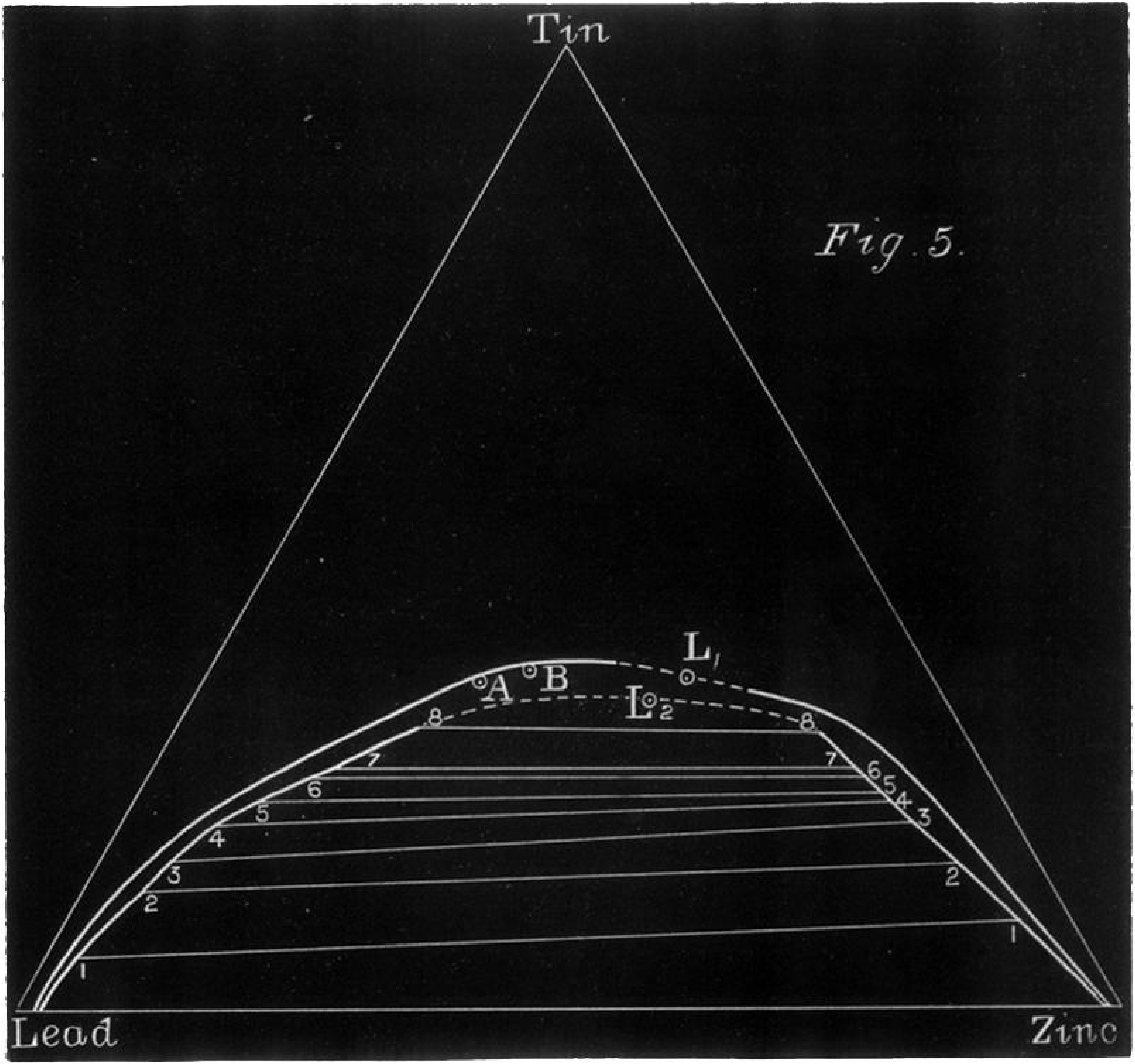


Fig. 5.

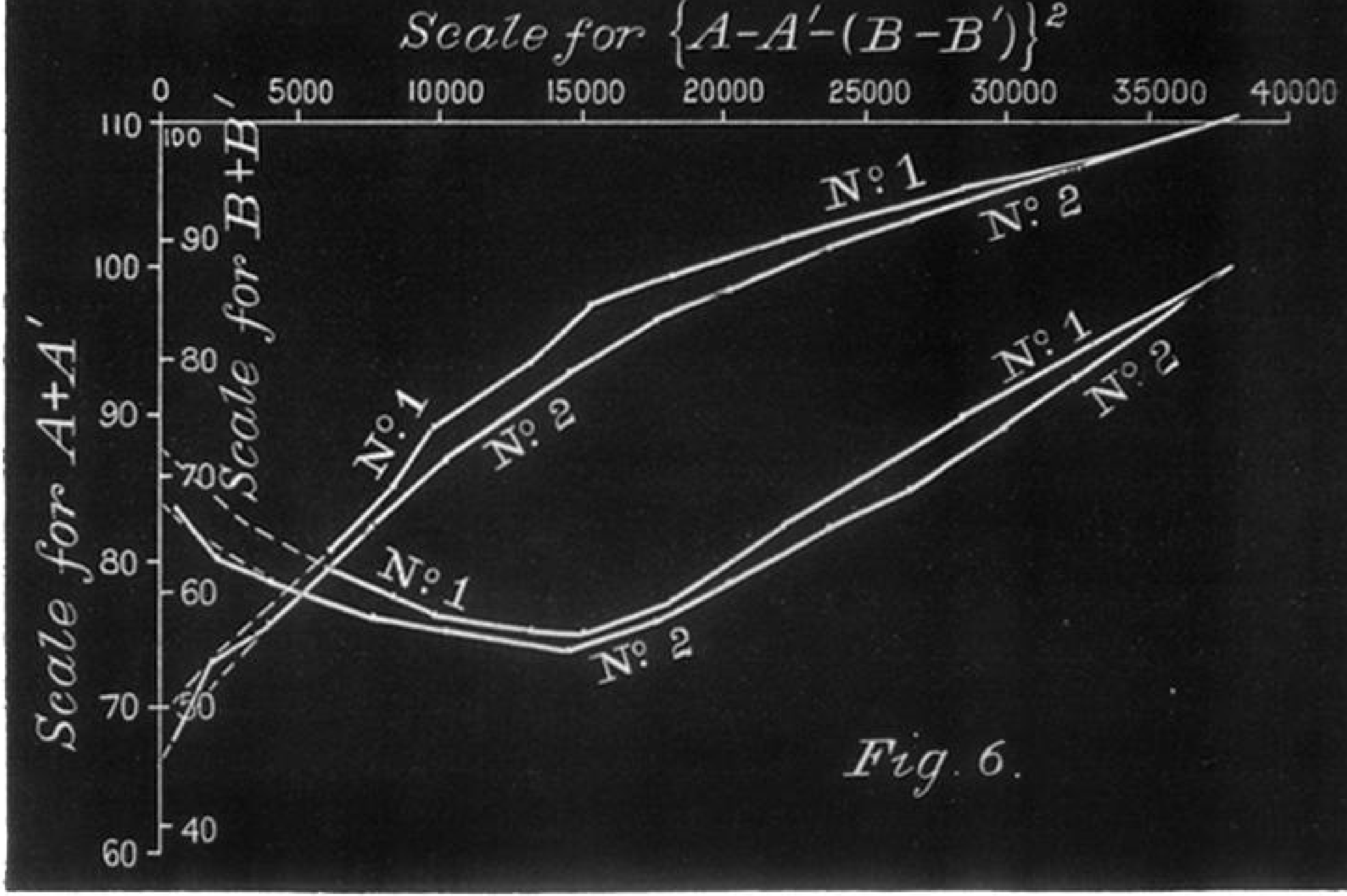

Scale for $\{A-A'-(B-B')\}^2$
0
5000
10000
15000
20000
25000
30000
35000
40000
Scale for A+A′
110
100
90
80
70
60
Scale for B+B′
100
90
80
70
60
50
40
N°. 1
N°. 2
N°. 1
N°. 2
N°. 1
N°. 2
N°. 1
N°. 2

Fig. 6.

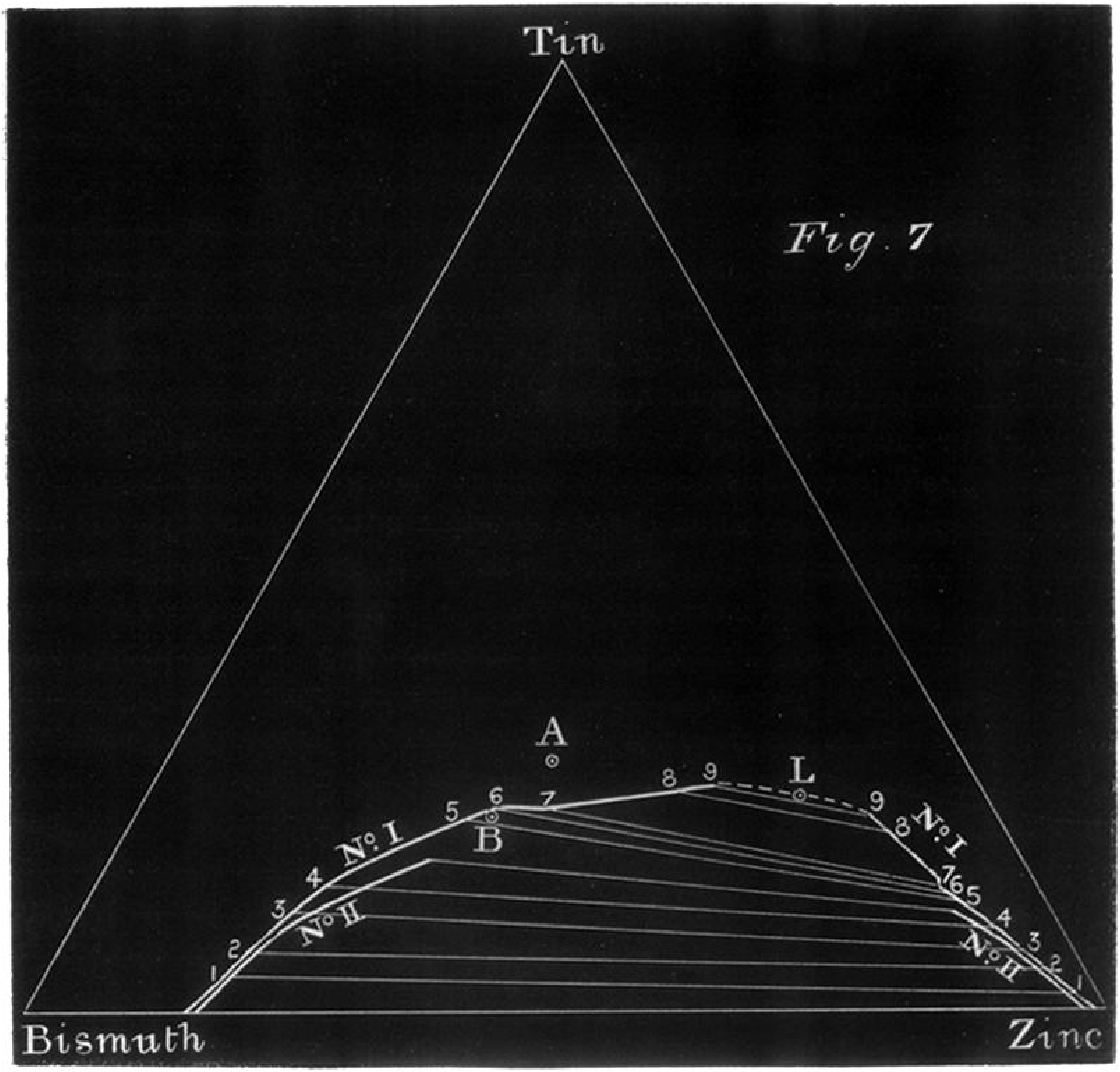


Fig. 7

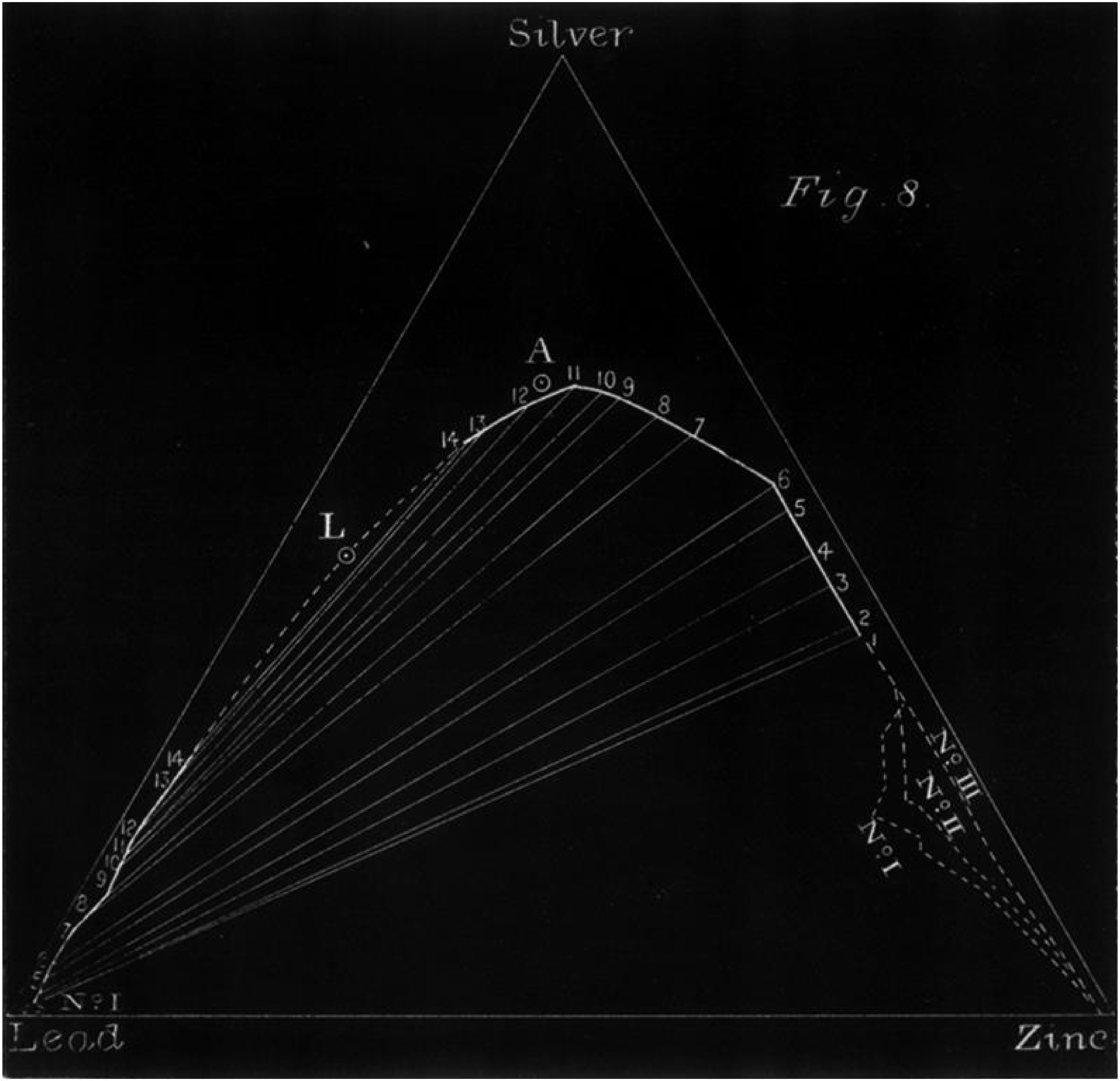


Fig. 8.

Silver
A
L
N°III
N°II
N°I
N°I
Lead
Zinc

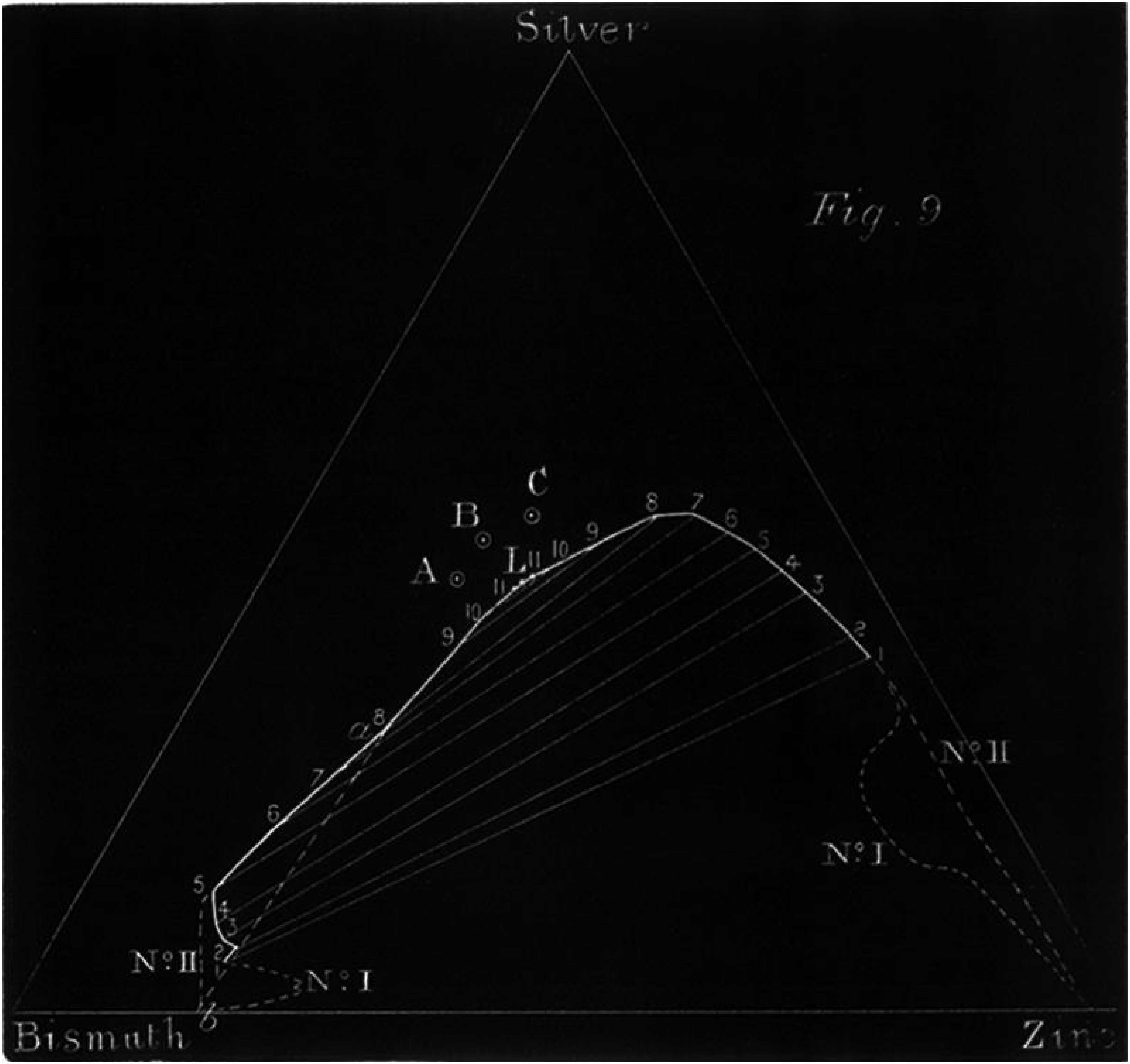


Fig. 9